Layered Double Hydroxides as Bifunctional Catalysts for the Aryl Borylation under Ligand-Free Conditions

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Abstract: Organic derivatives of boron, such as boronic esters and acids, are important precursors for a wide range of environmental, energy, and health applications. Several catalytic methods for their synthesis have been reported, even though with the use of toxic and structurally complex ligands. Herein, we demonstrate preliminary studies envisaging the synthesis of boronic esters from an inexpensive catalytic system based on Cu/Al layered double hydroxides (LDH) in the presence of Na_2PdCl_4. The Cu/ Al LDHs were prepared according to coprecipitation method and characterized by X-ray diffraction (XRD) (with Rietveld refinement) to evaluate the contamination with malachite and other phases. Preliminary catalytic results suggest that pure Cu/Al LDH has potential for the borylation of aryl iodides/ bromides in the absence of base. Indeed, a synergic effect between copper and palladium is possibly related to the catalytic efficiency.

Keywords: boronic esters; borylation; Suzuki–Miyaura; layered double hydroxides; copper; palladium

1. Introduction

Organoboron compounds have received great attention in last years due to significant impact in analytical [1], technological [2], and medicinal fields [3]. Particularly, low-weight compounds containing boronic acid/ester moieties have played an important role in the synthesis of new hybrid materials, sensors and complex organic molecules, through synthetic protocols such as Suzuki–Miyaura reactions. However, mild and selective synthesis of boronic acids and esters still represent a challenge. In general, the classic reactions involving the generation of organometallics (e.g., arylmagnesium or aryllithium) followed by the reaction with a borate have been substituted by catalytic protocols [4]. Recently, new methods involving metal-free conditions have also been discovered [5,6]. However, most of them suffer from low reactivity/selectivity along with relatively high costs of the boron reagents. Some advantages of the catalytic protocols are the improved reaction selectivity and the possibility of the whole system reuse. Since the general steps for the catalytic synthesis of boronic acids and esters involve a sequence of oxidative addition and reductive elimination, several

semihomogenous or heterogeneous systems are described based on the employment of noble metals (e.g., Pd and Ir) as catalysts [7].

In 1995, Miyaura first reported the Pd-catalyzed aryl borylation protocol by using a phosphine-based catalyst—Pd(dppf)Cl$_2$—in the presence of KOAc for the activation of diboron reagent [8]. Since then, several efficient methodologies have been reported based on similar reaction conditions [9–11]. Recently, Ratniyom and coworkers [12] reported an efficient cooperative catalysis based on Pd(0)/Cu(I) in the presence of triphenylphosphine with good results towards aryl iodides and bis(pinacolate)diboron. However, the yields were very sensitive to the nature of the base and reduced drastically with the use of aryl bromides/chlorides.

Inorganic networks with basic properties represent one alternative to avoid the use of expensive ligands as well as strong bases in order to achieve the B–B bond activation. Mostly, bimetallic systems usually involve low loadings of a noble metal in combination with an early transition metal to allow a cost-effective, broader functional group tolerance, and scalable reaction condition. Layered double hydroxides (LDHs)—anionic clays also known as hydrotalcites—have a structure based on layers of bi- and trivalent metals hydroxides and interlayer spaces occupied by anions and neutral molecules [13], see Figure 1. They can be composed of a wide range of different metals and anions, which make them useful as anionic exchangers, flame retardants, catalysts, and supports for metallic nanoparticles [14], and have low-cost of synthesis and basic surface properties [15]. Silva and coworkers [16] previously reported a catalyst system based on Mg/Al LDHs, PdNPs, and cyclodextrins for the efficient Suzuki–Miyaura reaction between aryl bromides and arylboronic acids. Lately, Sreedhar [17] employed Cu/Al LDHs as catalysts in Ullmann reactions between aryl chlorides and amines. So far, cross-coupling with heterogeneous ligand-free Cu(II) based cocatalysts has not been reported to date in borylation reactions.
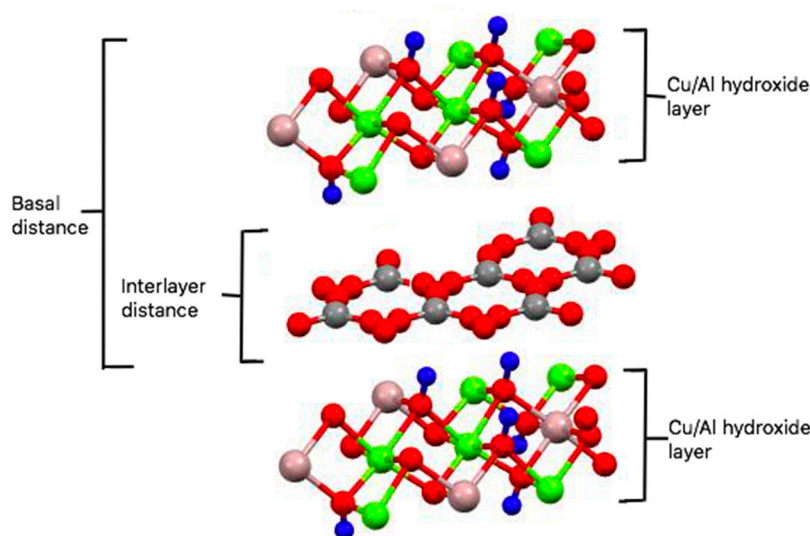

Figure 1. Representation of layered double hydroxide (LDH) hydrotalcite-like structure, with the Cu/Al hydroxide layers and the carbonate containing interlayer space. Cu → green, O → red, H → blue, C → grey, Al → light red.

In the present work, we disclosed Cu/Al LDHs as bifunctional cocatalysts in the presence of Na$_2$PdCl$_4$ for the borylation reactions between aryl halides and bis(pinacolato)diboron. The key points examined here are the influence of LDH purity and the catalytic conditions towards the reaction outcome.

2. Results

2.1. Synthesis and Characterization of Cu/Al LDH

A set of conditions were varied to accomplish the synthesis of the Cu/Al LDH. Figure 2 shows the X-ray diffraction (XRD) patterns of samples obtained using or not sodium carbonate as an additive. These diffractograms were refined using the Rietveld method in order to obtain the composition of phases. In addition, the refinement also afforded the unit cell parameters for LDH phase: these data are available in the supporting information file (Tables S1–S4). The LDH synthesized without sodium carbonate (Figure 2a) exhibited a XRD pattern composed of reflections from the mineral-like phases of gerhardtite ($Cu(OH)NO_3$, JCPDS-ICDD 01-082-1991), hydrotalcite ($Mg_{0.67}Al_{0.33}(OH)_2)(CO_3)_{0.165}(H_2O)_{0.48}$, JCPDS-ICDD 01-089-5434), and nitratine ($NaNO_3$, JCPDS-ICDD 00-036-1474). The LDH phase was obtained as a low crystallinity, minority phase with wide and low intensity peaks at 9.7° and 19.9°. The $Cu(OH)NO_3$ phase (gerhardtite) was obtained as the majority phase with the most intense peaks at 12.7°, 25.6°, 33.9°, 36.1°, 40.4°, and 42.9°. Finally, $NaNO_3$ (nitratine) was found as another minority phase, however showing a thin peak at $2\theta = 22.8°$, besides 29.4°, 31.8°, and 38.9°.
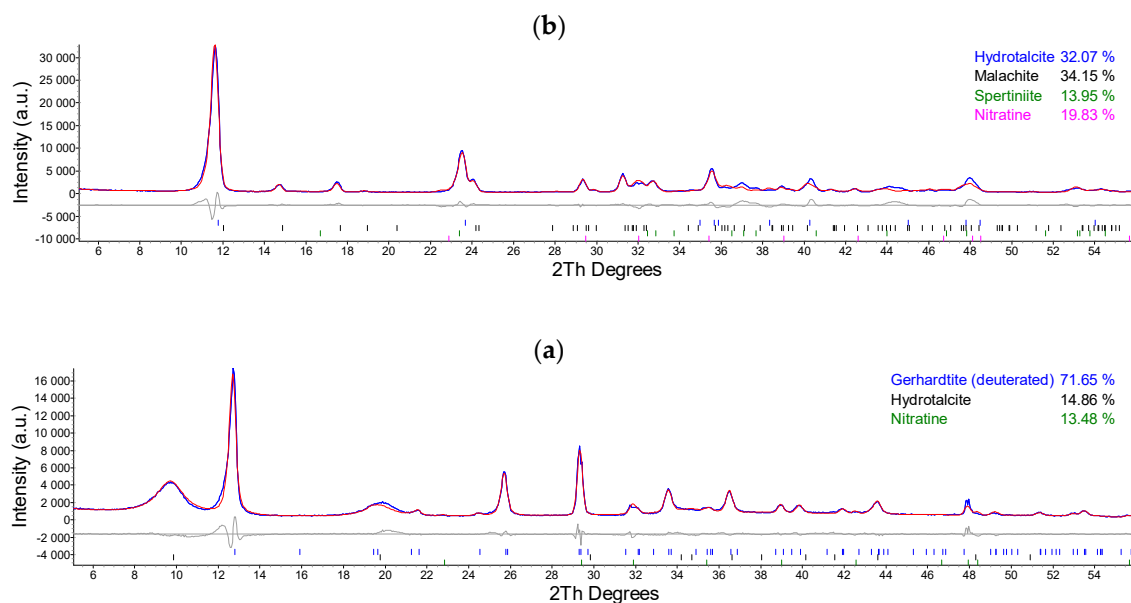

Figure 2. Rietveld-refined X-ray diffraction (XRD) patterns for Cu/Al LDH obtained (**a**) without and (**b**) with Na_2CO_3 dissolved in the precipitation agent solution.

In contrast, Figure 2b shows the XRD pattern for the sample synthesized using sodium carbonate. In this case, the majority phase was the layered double hydroxide with peaks at $2\theta = 11.6°, 23.5°, 35.6°$, 39.5°, and 47.0°. Another significant phase was malachite ($Cu_2(OH)_2CO_3$, JCPDS-ICDD 01-075-1163) related to the peaks $2\theta = 11.9°, 14.7°, 17.5°, 24.0° 29.7°, 31.7°, 32.6°$, and 35.4°. As minority phases, it was found that spertiniite ($Cu(OH)_2$ JCPDS-ICDD 01-080-0656) related to peaks at $2\theta = 16.7°, 23.8°$, 34.0°, 35.9°, and 39.8°, and nitratine with peaks at $2\theta = 22.8°, 29.4°, 31.8°$ and 38.9°.

Regarding the LDH unit cell parameters (Table S1, supporting information), both XRD were refined as having a rhombohedral crystal system and belonging to the R-3m spatial group. However, the sample synthesized without carbonate presented the biggest unit cell dimensions (a = 3.039 Å and c = 26.921 Å against a = 2.979 Å and c = 22.519 Å for the carbonate Cu/Al LDH), which means that an expanded structural network was obtained.

The addition of sodium carbonate to the reaction medium allowed obtaining LDH as the main phase, but did not avoid forming malachite, a by-product. Still, it was decided to use the carbonate salt dissolved in the precipitation agent solution in the fore coming tests.

In the next set of experiments the LDH precipitation pH and postsynthesis work-up were evaluated.

The precipitation pH was varied between two values, 8 and 10, which are the most used in LDH synthesis. The XRD patterns for both samples are presented in Figure 3. Figure 3a evidences the refined XRD pattern for the LDH precipitated at pH = 8, which, compared to that of Figure 3b, related to LDH precipitated at pH = 10; thus pH is not a significant parameter in the synthesis. This is also supported by strong similarities of unit cell dimensions between these two samples (Table S2, supporting information). Therefore, a pH of 8 was chosen as the working pH in the next tests.
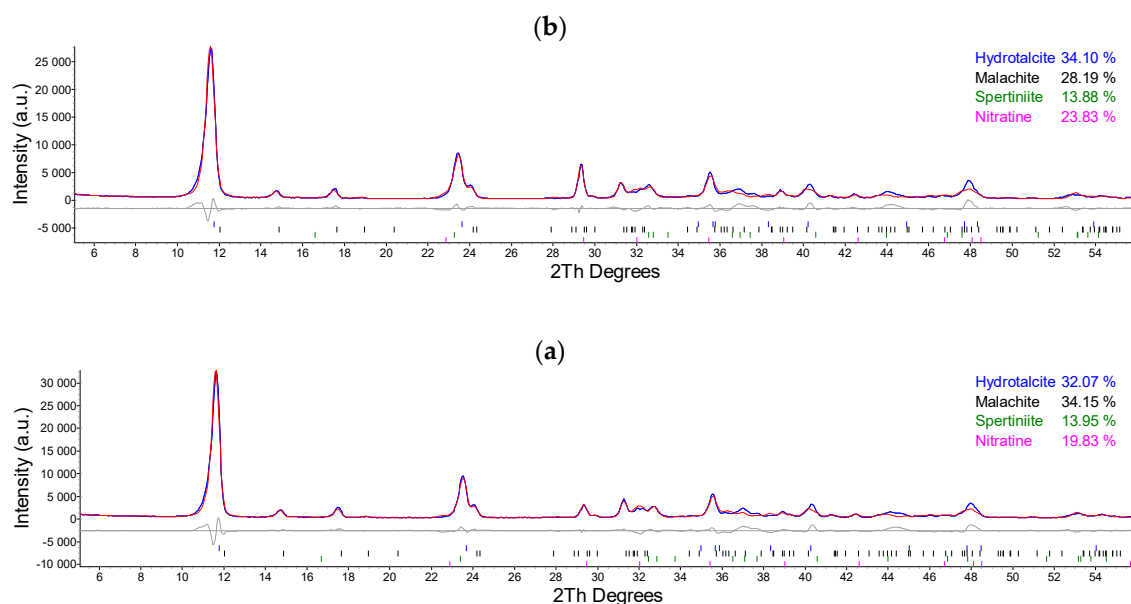

Figure 3. Rietveld-refined XRD patterns for Cu/Al LDH obtained at (**a**) pH = 8 and (**b**) pH = 10.

In all experiments the LDH postsynthesis work-up proceeded using centrifugation, but one sample was isolated using filtration. Their refined XRD patterns are shown in Figure 4. Concerning the unit cell dimensions, no significant differences between these two samples can be perceived (Table S3, supporting information) As evidenced when nitratine phase percentages are compared the centrifuged sample (Figure 4a) it exhibits 5-fold more $NaNO_3$ than the filtrated solid (Figure 4b), which implies that the postsynthesis work up is an important parameter to be aware of.

To reinforce that postsynthesis steps are very important one last sample was synthesized following the conditions established in the present study; however, this LDH was submitted to washing, using organic solvents (EtOH/Acetone). Its refined XRD measurements are presented in the Figure 5. The calculated unit cell parameters show no significant differences from those previously shown (Table S4, supporting information). In the phase distribution it is clearly observed that the malachite % dropped from 31.93% (Figure 4b) to 10.23% (Figure 5), increasing LDH % from 47.92% to 65.70%.

Besides, the XRD peaks shown in Figure 5 appear wider and less intense than those in Figure 4b, for instance. According to the Full Width Half the Maximum (FWHM) criterium used in the Scherrer formula, the mean crystal size evolved from 21 nm (for samples of Figures 3 and 4) to 14 nm, signaling a decrease in crystallinity upon postsynthesis treatment, such as washing with organic solvents.

To evaluate the effect on the borylation reaction, catalytic tests were carried out by using malachite and LDH as catalysts.
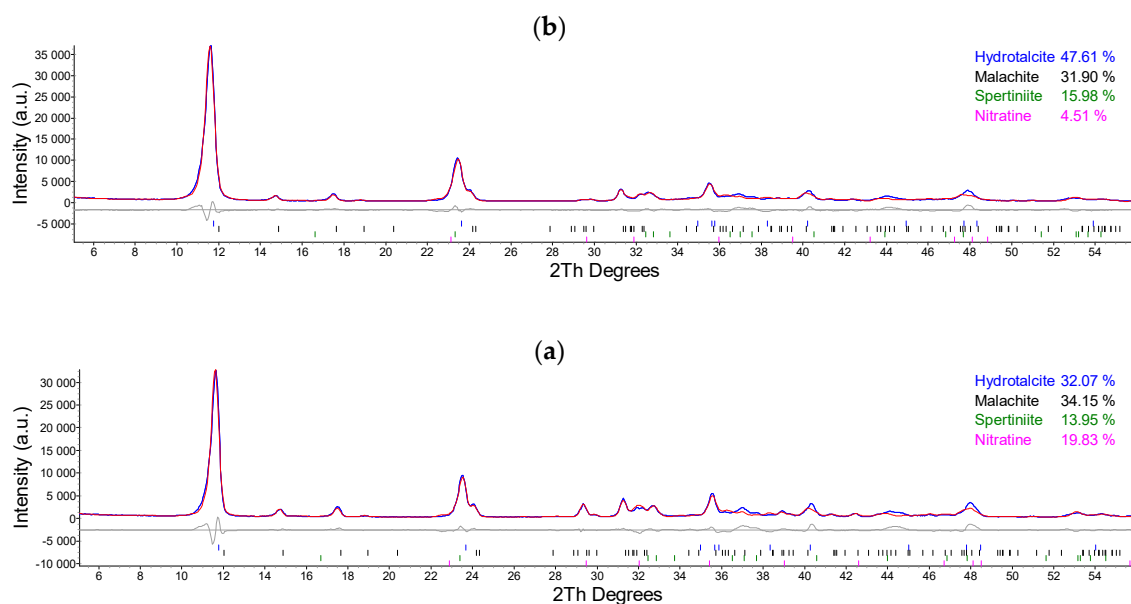
Figure 4. Rietveld-refined XRD patterns for Cu/Al LDH obtained after (**a**) centrifugation and (**b**) filtration.
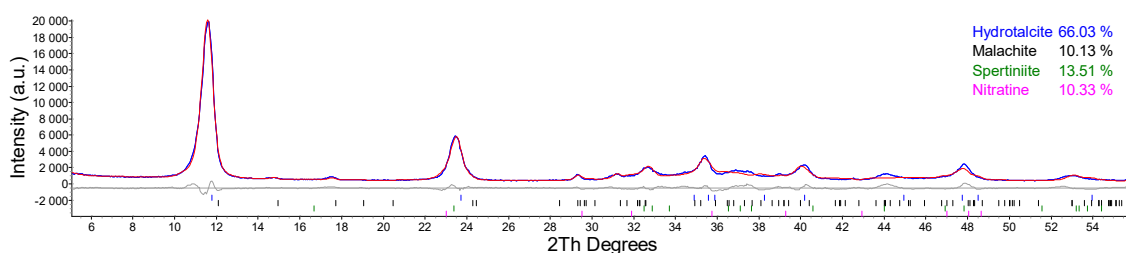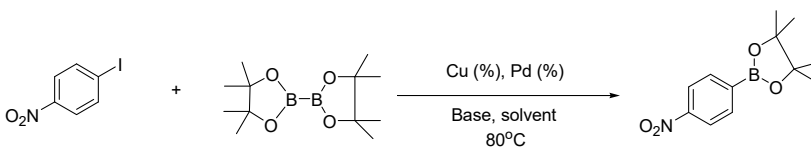

Figure 5. Rietveld-refined XRD pattern for Cu/Al LDH obtained after washing with ethanol and acetone.

2.2. Synthesis of Aryl Boronic Esters Employing Cu/Al LDH Catalyst

The reaction between bis(pinacolato)diboron, (B(pin)$_2$) and 1-iodo-4-nitrobenzene was taken as a model. Initially, purified Cu/Al LDH and malachite were evaluated as catalysts with acetonitrile as solvent. From these data, it is possible to confirm that malachite did not show catalytic activity towards the borylation reaction. To evaluate the copper loading, we used the LDH composition according to the method previously described by our group [18]. It was observed that both copper-based catalysts were not able to catalyze the reaction (Table 1, entries 1 and 2). Similarly, the use of Na$_2$PdCl$_4$ as the sole catalyst was ineffective (Table 1, entry 3). Indeed, addition of CuSO$_4$ in combination with Na$_2$PdCl$_4$ did not react under this condition (Table 1, entry 4). The comparison of the Pd precursor led us to evaluate a semihomogeneous system composed of palladium nanoparticles (PdNPs) stabilized by cyclodextrins (Table 1, entries 5 and 6). Our research group have already described this catalytic system to the carbon–carbon cross-coupling reactions [19]. However, it was not observed significant conversion even when using acetonitrile. Remarkably, the addition of 2 mol% Na$_2$PdCl$_4$ in the presence of LDH (30 mol% Cu) allowed a yield of 98% of the expected product (Table 1, entry 7). Since the positive effect could be related to the LDH structural and compositional properties, we also tested the most common Mg/Al LDH in the presence of CuSO$_4$ and Na$_2$PdCl$_4$, which rendered a good yield (Table 1, entry 8). Having in mind that the Cu/Al LDH is an anionic exchanger, it has been tested a [PdCl$_4$]$^{2-}$ exchanged Cu/Al LDH, and surprisingly, the yield obtained was significantly lower, 35% (Table 1, entry 8).

Table 1. Survey of reaction condition.

Entry	Catalyst System	Cu (mol%)	Pd (mol%)	Yield (%) [1] of 3
1	LDH	30	-	29%
2	Malachite	30	-	<5%
3	Na_2PdCl_4	-	2	<5%
4	PdNPs-CD	-	2	<5%
5	PdNPs-CD	-	2	<5%
6	Na_2PdCl_4/CuSO$_4$	30	2	<5%
7	Na_2PdCl_4/LDH	30	2	98%
8	Na_2PdCl_4/CuSO$_4$/LDH [2]	30	2	77%
9	Na_2PdCl_4/LDH [3]	30	2	35%
10	Na_2PdCl_4/LDH	15	2	54%
11	Na_2PdCl_4/LDH	7.5	2	42%
12	Na_2PdCl_4/LDH	3.75	2	26%
13	Na_2PdCl_4/LDH	30	1	46%
14	Na_2PdCl_4/LDH	30	0.5	42%
15	Na_2PdCl_4/LDH	30	0.05	23%
16	Na_2PdCl_4/LDH [4]	30	2	<10%
17	Na_2PdCl_4/LDH [5]	30	2	<10%
18	Na_2PdCl_4/LDH [6]	30	2	<5%
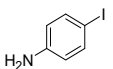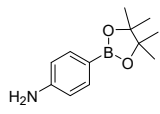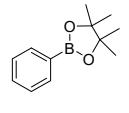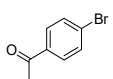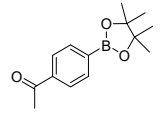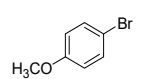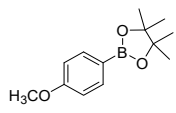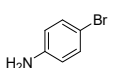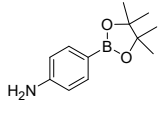
[1] Determined by gas chromatography–mass spectrometry (GC-MS); [2] Use of Mg/Al LDH, CuSO$_4$ and Na_2PdCl_4; [3] LDH intercalated with Na_2PdCl_4; [4] solvent = THF; [5] solvent = dioxane; [6] Addition of Cs$_2$CO$_3$.

In order to see the effect of copper in the reaction, we have tested different copper loadings (Table 1, entries 10–12). According to the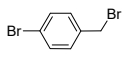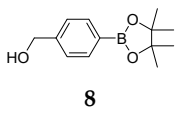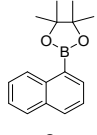 results, a relatively high loading of copper has shown to be the most adequate for a high conversion (Table 1, entry 7). Similarly, to verify the influence of the Pd loading it was varied from 2 to 0.05% under the same conditions (Table 1, entries 13–15). In this case, 2 mol% Pd was necessary to keep an acceptable turnover. Analogously to Cu%, it was observed a direct relationship between the conversion rate and the Pd%. With the aim of evaluating the effect of noncoordinating solvents, THF and dioxane (Table 1, entries 16 and 17) were also tested under the conditions described in Table 1, entry 3. Surprisingly, no appreciable yield of the product was observed in both cases. Additionally, the use of base hampered the reaction (Table 1, entry 18).

Since the above results demonstrated that the catalytic system based on Cu/Al LDH and Pd(II) can be efficiently used for the borylation of an aryl iodide under ligand-free conditions, we carried out preliminary reactions with some aryl halides in order to examine its applicability. In this case, we have tested the influence of electron-withdrawing/donating groups substituted in the aromatic core. By considering their comparatively low-cost and availability, we have mainly focused on the evaluation of the reactivity of aryl bromides.

In general, it was possible to note an influence of the electron-withdrawing/ donating capabilities of the substitutional groups. Remarkably, it was evident that the strongly electron-donating amine group did not favor the reaction in both cases (Table 2, entries 1 and 5). In general, the absence of a substituent led to small yields.

Table 2. Preliminary scope for the borylation reaction catalyzed by Cu/Al LDH and Na_2PdCl_4 [1].

Entry	Aryl Halide	Product	Yield (%)
1		**4**	<10
2		**5**	<10
3		**6**	55
4		**7**	98
5		**4**	<10
6		**8**	30
7		**9**	45

[1] Determined by GC-MS.

Encouraged by the preliminary results, we next investigated whether this catalyst could have recycling potential. In such case, it could shed a light on the behavior of Cu/Al LDH as a reservoir or as real catalytically active species. However, attempts to recover the material after reaction work up failed.

3. Discussion

Malachite is a common second phase present in Cu/Al LDH synthetic samples [20–26], and it is known to affect the general properties of the LDH, such as its catalytic properties [23–25]. In most cases, it arises from the need to use sodium carbonate as a precipitation co-agent, otherwise LDH is not formed as the majority phase, as observed in Figure 2a. The way the unit cell dimensions obtained for this phase (Table S1, supporting material) evidenced an expanded network in comparison to the carbonate containing LDH phases. This can be understood in terms of attraction electrostatic forces acting between layer and interlayer parts of the material that permit to pack more efficiently when CO_3^{2-} instead of NO_3^- is used as the intercalated ion.

Some authors in the literature have tried to eliminate the malachite impurity by a number of different approaches.

Muñoz et al. [23] sought for pure Cu/Al LDH in order to obtain its calcined-oxide derivative to catalyze the reduction of NO and CO gases. Through coprecipitation method synthesis they were able to verify that precursors solutions with lower concentrations prevented the formation of malachite, and that the oxide derived from malachite-free LDH showed better catalytic results than the derived from impure LDH. Gao et al. [24] synthetized Cu/Zn/Al/Zr LDH in order to obtain its calcined oxide for the catalysis of CO_2 hydrogenation, and also found that catalysts with malachite prior to the calcination presented worse catalytic activity than the ones without the contamination. Both Muñoz and Gao agree that higher ratios of Cu/Al induce the formation of malachite. Ichikawa et al. [25] tried a different way to obtain noncontaminated Cu/Al LDH: they used a coprecipitation method followed by an aging process at 90 °C under air bubbling for 1 h. They stated that this process helped to smooth the crystallization process removing the excess of CO_3^{2-} ions. They also found that the calcined oxide derived from the pure Cu/Al LDH was a better catalyst to the conversion of acrylonitrile to acrylamide than the contaminated one. Recently, Qu et al. [26] reported a new mechanochemical synthesis method for Cu/Al LDH, in which they dry milled $Cu_2(OH)_2CO_3$ and $Al(OH)_3$ at a planetary ball mill for 2 h at 600 rpm, producing an amorphous solid mixture that was treated in aqueous medium at room temperature under magnetic stirring for 4 h, producing a pure Cu/Al LDH.

Another important feature is the presence of nitratine ($NaNO_3$) in the phase mixture composition after LDH synthesis. Firstly, this phase arises from the combination of sodium of NaOH solution and nitrate from salt precursors of Cu^{2+} and Al^{3+}. However, considering sodium nitrate is soluble in aqueous medium, it is not clear how this phase coprecipitates with LDH. Figure 4 gives a hint: the centrifugation process leads to 5-fold increase of nitratine% in the phase mixture composition. In addition, Figure 5 points to a decrease by half of this phase percentage guaranteed by washing with EtOH/Acetone. Therefore, the combined use of filtration and washing in the postsynthesis work-up of LDH is beneficial for this catalyst.

The catalytic conditions studied for the borylation model reaction were initiated with an activated aryl iodide since electron-withdrawing groups are known for the accelerated effect on the reaction rate [7]. Under the basic conditions of the classical Pd cycle, it is assumed that the higher the Ar-Pd(II)-X electrophilicity, the faster the transmetallation with bisorganodiboron. In fact, the results pointed to a high catalytic conversion by using 4-iodonitrobenzene as an electrophile. To evidence the clean and selective conditions for the borylation reaction, the crude ^{1}H NMR spectrum of **3** is presented in the Supporting Information. A relatively high copper loading was, however, necessary to increase the substrate conversion. As pointed out, this fact has already been observed by Ratnyom [12] and other groups [13] but involving a typically homogeneous catalytic system based on Cu or Pd/Cu combined with phosphines. Regarding the usual organometallic mechanism, it is interesting to note that the LDH surface is possibly responsible for the presence of basic species involved in the preactivation step. The addition of base, however, was detrimental to the reaction, suggesting a partial decomposition of the LDH structure.

Even though the cooperative catalysis of Pd and Cu was already reported in some recent works, the ligand-free condition has been scarcely explored mostly because of the difficult electronic tuning towards the transmetallation step even though the soft coordination of acetonitrile cannot be ruled out. However, the surprising fact here is related to the superior activity of a heterogeneous layered Cu matrix, which allowed high substrate conversion and product selectivity in the reaction model. In detriment, common copper salts, such as the basic copper carbonate (malachite), were ineffective under the same conditions, indicating that the chemical environmental around copper is decisive to the reaction outcome even in the presence of palladium. This fact could be reinforced when testing Mg/Al LDH in the presence of $CuSO_4$ and Na_2PdCl_4 that resulted in an inferior product yield compared to the same catalytic conditions by using the Cu/Al matrix.

In addition, the preliminary scope of the method showed an unclear electronic effect of substituents: apparently, the reaction is favored by both electron-donating and -withdrawing groups but, intriguingly, it was not the case for the amine substituent. It is conceivable that a hybrid mechanism is operative with the moderate to low yields of α-naphtyl, 4-bromobenzyl and phenyl bromides arising from a predominant oxidative addition modulation. However, the low reactivity of bromobenzene was intriguing. We presume the occurrence of possible alternative pathways (e.g., Ullmann-type reaction and hydrodehalogenation) in minor extension but the solubility factor cannot be ruled out. Indeed, the role of LDH matrix as a catalytic reservoir of active Cu species can be considered based on experiments with coordinating solvents [27]. According to the frustrated catalyst recycling attempts, it is also possible that acetonitrile act as a moderate LDH exfoliation agent. On the other hand, the effect of $PdCl_4{}^{2-}$ intercalation in LDH seems to slow down the possible Pd(II) reduction. Lastly, $(Bpin)_2$ seems to be involved in the reduction of Pd(II) species, as suggested by the solution darkening according to visual inspection.

Taken together, these results suggest that a synergic effect between the Cu(II) and Pd(0) species can arise from a combination of factors related to the electronic effects on substrate along with the chemical environment of both metals.

A schematic view containing some of these effects is shown in Scheme 1.
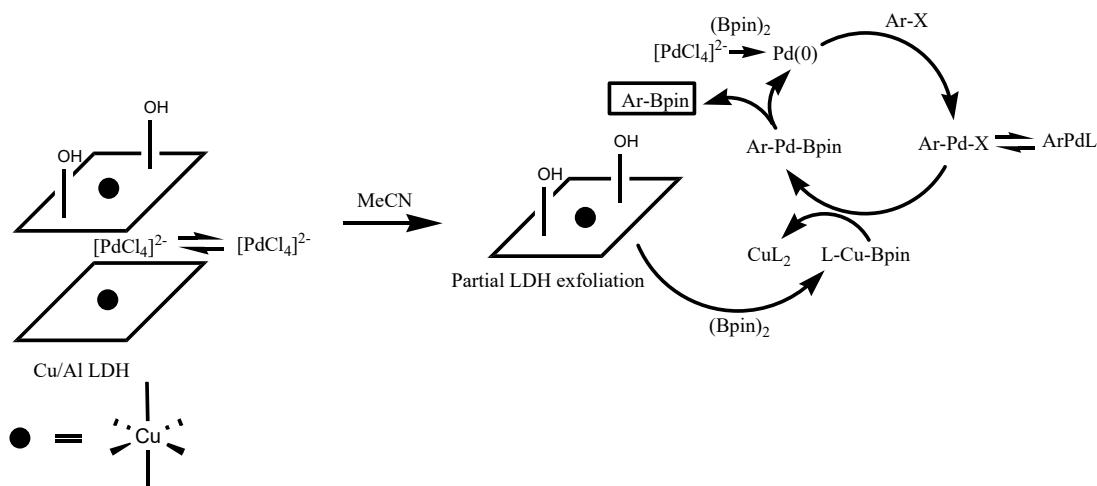
Scheme 1. Proposed mechanism for the Pd and Cu-catalyzed aryl borylation in the presence of LDH.

4. Materials and Methods

All the reactants and solvents in this work were commercially acquired and used without previous purification.

The powder X-ray diffractograms were recorded by a diffractometer Panalytical X´Pert PRO MPD (Malvern Panalytical Ltd., Royston, United Kingdom), with generator of Cu X-ray (λ = 1.5418 Å), line focus (1.8 kW), universal Theta-2Theta goniometer with 240 mm radius, divergence slit fixed $\frac{1}{2}°$, flat-diffracted beam monochromator, and proportional detector Xe with 40 kV of tension and 40 mA of current in the X-ray tube. The samples were analyzed self-supported in aluminum sample holder and used under the Bragg–Brentano geometry; it used ranges between 5° < 2θ < 70°, with 0.05° step and 2.5 s per step.

The calculation based on the Rietveld Refinement applied in this work, through the program TOPAS academic V5.0 (Coelho Software, Brisbane, Australia), was based on the Fundamental Parameters Approach, based on the instrumental parameters with background correction. If necessary, the following parameters were refined; unit cell dimensions, sample height displacement, zero-shift, weight fraction (scaling), preferred orientation, atomic species/substitutions, atomic coordinates, site occupancies, thermal displacement parameters, crystallite size, and lattice strain.

All the organic products were characterized by ^{1}H and ^{13}C NMR spectroscopy (Bruker Analytics, Berlin, Germany).

4.1. Synthesis of the Cu/Al Layered Double Hydroxides

The Cu/Al layered double hydroxides (Cu/Al LDH) and $Cu_4Al_2(OH)_{12}CO_3\cdot4H_2O$, were synthetized using a constant pH method: one aqueous solution of $Cu(NO_3)_2\cdot3H_2O$ (0.225 mol·L^{-1}) and $Al(NO_3)_3\cdot9H_2O$ (0.075 mol·L^{-1}) and other of NaOH (0.50 mol·L^{-1}) and, alternatively, Na_2CO_3 (0.15 mol·L^{-1}), were added (40 mL each) simultaneously by continuous dropping to 40 mL of a NaOH solution (pH = 8 or 10), under magnetic stirring at room temperature. The pH was maintained during the process. A blue slurry was formed, which was then filtrated or centrifuged and dried at room temperature. The filtrated material was alternatively washed with ethanol:acetone 1:1 volume mixture.

### 4.2. Synthesis of Boronic Esters Employing Palladium Nanoparticles

The synthesis of PdNPs followed method described by Senra et al. [19], Scheme 2. At first, 1 mL of a Na_2PdCl_4 0.005 mol·L^{-1} aqueous solution was mixed with 69 mg of β-cyclodextrin in a 10 mL glass flask and the mixture was kept at 70 °C for 1 h under magnetic stirring. Then, it was added to the flask 0.25 mmol of 1-bromo-4-methoxybenzene, 0.25 mmol de bis(pinacolato)diboron, 0.375 mmol of K_2CO_3, and 2 mL of solvent (ethanol/H_2O 50% or acetonitrile). The system was kept at 70 °C for 24 h, and then the reaction mixture was extracted with dichloromethane and NaCl aqueous saturated solution (1:1). After the extraction, the mixture was dried with anhydrous sodium sulfate and evaporated under reduced pressure.

R = H, OCH$_3$
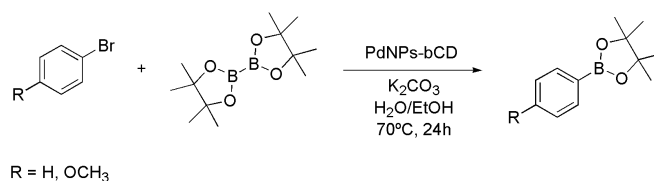
Scheme 2. Preliminary reaction.

4.3. Synthesis of Boronic Esters Employing Na_2PdCl_4/Cu/Al LDH

Into a 5-mL screw cap flask was added 0.9 mmol de bis(pinacolato)diboron, 0.6 mmol de 1-iodo-4-nitrobenzene, 2 mL of solvent, and 0.15 mmol (Cu) of LDH/Pd or 0.15 mmol (Cu) of Cu/Al LDH and 2 mL of Na_2PdCl_4 0.005 mol·L^{-1} aqueous solution, Scheme 3. In the latter, the percentage of palladium varied from 2% to 0.5%. The system was kept at 70 °C for 24 h under magnetic stirring, and its extraction was done as described in Supporting Information.
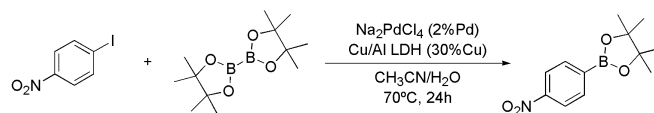
Scheme 3. Model reaction.

5. Conclusions

Cu/Al LDH had some synthesis parameters evaluated in order to produce the least quantity of by-products. For such material, the list of contaminants includes the mineral-like phases malachite, spertiniite, and nitratine. The catalytic system based on the least-contaminated LDH heterogeneous matrix and aqueous Na_2PdCl_4, under ligand-free conditions, showed efficient catalytic properties in the borylation reactions by using bis(pinacolato)diboron as boron precursor. This catalyst system can be a promising low-cost alternative for use in classical homogeneous phosphine-based systems.

Additional experiments to investigate the possible reaction intermediates and their correlation with the LDH structure are under investigation and will be reported in due course.

Author Contributions: L.C.L.L.F.S. conducted all the borylation reactions. V.A.N. prepared the catalysts. V.S.R. and J.B.d.C. conducted the XRD analysis and the Rietveld refinements. R.S.F.S. and A.A.d.S. conducted the product characterization. L.F.B.M. and J.D.S. supervised the work and wrote the paper.

Conflicts of Interest: The authors declare no conflicts of interest.

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